Materials Science in Semiconductor Processing 59 (2017) 10–17

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Deep Diffusion of Phosphorus in Silicon using Microsecond-pulsed Laser Doping☆

Som Mondal*, Chetan Singh Solanki

Department of Energy Science & Engineering, Indian Institute of Technology Bombay, Mumbai 400076, India

ARTICLE INFO

Keywords:
Deep diffusion
EBIC
Junction depth
Laser doping

ABSTRACT

Deep diffusion of phosphorus atoms in monocrystalline silicon using laser doping process has been studied in this work. A pulse modulated CW fiber laser of wavelength 1070 nm with microsecond pulses has been used to diffuse phosphorus from pre-deposited spin-on-dopant film. The surface and cross-sectional morphology has been studied using SEM and AFM. The concentration-depth profiling was done using PP-TOFMS. Deep junctions of more than 10 µm have been obtained under various laser doping conditions while a maximum junction depth of 51.3 µm has been obtained through optimization. Diffusion depth enhancement is made possible by increasing the pulse length and reducing laser scan speed. Laser doping led to formation of n^+ region with surface concentration varying in the range of 3×10^{20}–5×10^{20} cm^{-3} for varying scan speed. Cross-sectional TEM and diffraction studies on laser irradiated samples show presence of only monocrystalline silicon phase after laser induced melting and solidification.

1. Introduction

LASER assisted processes are attractive for large scale silicon solar cell production as addition of simple cost-effective steps in the production line is required to achieve finite efficiency improvement. By application of different laser assisted processes, solar cell efficiencies in the range of 19–20.5% on Czochralski (Cz) substrate have been reported [1–3]. The key advantage of any laser assisted process is that laser can be irradiated on selective area of a solar cell during fabrication. Laser assisted processes such as edge isolation [4,5], dielectric ablation [6,7], laser doping [8], laser fired contacts [9], etc. have been proven to be suitable for industrial solar cell production.

Lasers with short wavelengths like 355 nm and short pulse lengths, in the range from nanoseconds to picoseconds, are ideal for localized strong absorption in silicon or dielectric layers. These lasers are suitable for ablation processes like edge-isolation, via-hole drilling and dielectric layer patterning. However, short pulsed green laser of wavelength 532 nm is also used effectively for such processes [10]. Lasers with 532 nm or 1064 nm and short pulse lengths are suitable for selective emitter and laser fired contacts fabrication [9,11,12]. However, UV laser have been used for laser doping, as well [13,14].

Laser doping of dopant atoms in silicon to form p-n junction has been reported as early as in 1968 [8]. In recent times, the process has been used for fabrication of selective emitter on a relatively low-doped emitter sheet (R_{sh}~ 80–100 Ω/□) to minimize the carrier recombination and dark saturation current density (J_{0e} < 30 fA/cm^2) [15]. The doping may be performed both before and after dielectric layer deposition with suitable metallization scheme [12,16]. Laser doping has also been employed to demonstrate the fabrication of full area emitter by scanning the laser beam [17,18]. Laser doped selective emitters using dopant sources such as spin-on-dopant [11], precursor gas [19], phosphosilicate glass formed after diffusion [12], phosphoric acid [20] etc. have been demonstrated, wherein the choice of the dopant source depends on the subsequent metallization scheme.

Laser doping is used for standard p–n junction formation and for selective emitter fabrication. In standard p-n junctions, the depth of diffused junction is typically around 500 nm while the junction depth of selective emitter fabricated by laser doping has been reported to be in range of few tenths of nanometers to few microns [8,21,22]. The junction depth achieved by laser doping depends on the process parameters. Use of laser doping process for deep diffusion or fabrication of junction which is deeper than few microns has not been of great interest in solar cell research as solar cell structures do not necessarily require such deep junctions. However, deep junction, if possible to fabricate, can be useful in better carrier collection from the bulk region. Recent work by Hallam et al. has presented how deep junction formation can be useful for the conventional solar cell fabrication scheme [23].

☆ This work is supported by National Centre for Photovoltaic Research and Education (NCPRE), funded by MNRE, Govt. of India.
* Corresponding author.
E-mail addresses: s_mondal@iitb.ac.in (S. Mondal), chetanss@iitb.ac.in (C.S. Solanki).

http://dx.doi.org/10.1016/j.mssp.2016.11.011
Received 13 June 2016; Received in revised form 14 October 2016; Accepted 8 November 2016
1369-8001/

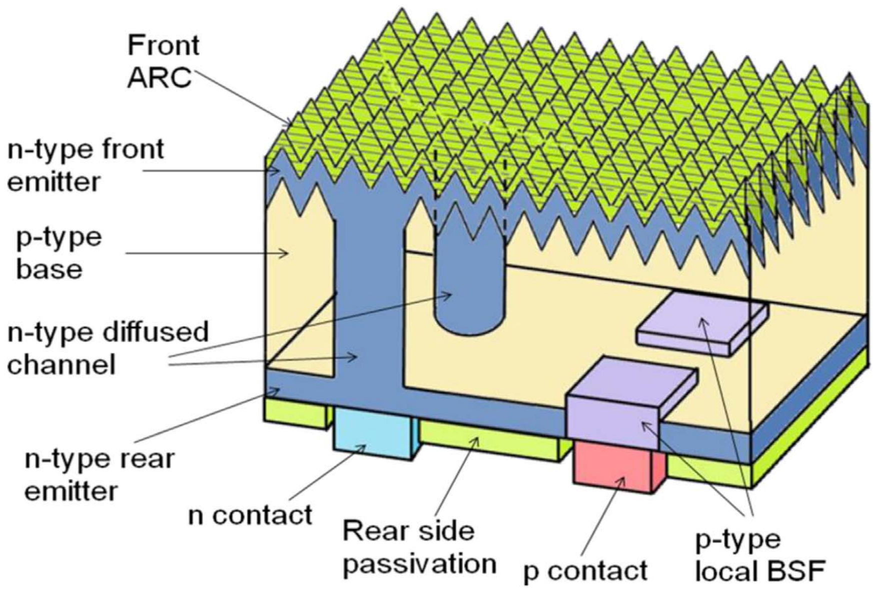

Fig. 1. Proposed emitter wrap-through solar cell structure with diffused channel being the main feature requiring study of deep diffusion..

Similarly, deep junction would also be useful for carrier separation in emitter wrap-through (EWT) solar cell structure with diffused channels which was proposed in an earlier study by the authors [24]. The proposed solar cell structure is schematically presented in Fig. 1. The advantage of deep diffused channel over metal filled via holes in EWT structure is that there is no constraint on separation between the channels (or via-holes) and the channels can be as close as required. The mechanical strength of the proposed structure can be better than conventional EWT structure in which fabrication of multiple holes may lead to significant material ablation. In addition, the carriers separated at the front junction of the cell can conduct through the entire cross-section of the channel of the proposed structure while carriers can conduct through the via-emitter only, in case of partially metal filled via in conventional structure. These advantages of the proposed structure can reduce the fill factor loss that is normally encountered in conventional EWT structure. Apart from solar cells, fabrication process of such ultra-deep junction may also become highly useful to conceptualize or demonstrate other silicon based microelectronics devices in future.

This study is, thus, aimed at achieving junction depth of several tenths of µm using laser doping process. A pulse-modulated Continuous Wave (CW) laser was used to diffuse phosphorus atoms in silicon. Sheet resistance, surface morphology, concentration-depth profiles, junction depth were studied and the results are presented in this paper. The depths of the diffused junctions were obtained using Plasma Profiling Time of Flight Mass Spectrometer (PP-TOFMS) and scanning electron microscopy electron beam induced current imaging (SEM-EBIC) techniques and are presented in this paper.

2. Experimental details

P-type polished Cz silicon wafers of resistivity 4–7 Ω cm and < 100 > orientation were used as substrate throughout this work. The wafers were cleaned in RCA solution to remove surface contaminations. Phosphorus spin-on dopant (Filmtronics Inc.) was then spin-coated onto the polished clean surface of the wafers. The spin-on dopant (SOD) coating was done at 3000 rpm for 30 s. After spin coating, the wafers with phosphorus film were heated on a hot-plate at 250 °C for 15 min to evaporate the organic solvent. The dopant film formed in the process acts as a source of phosphorus for subsequent laser doping. The SOD film is highly dependent on the local atmospheric condition and it is hygroscopic in nature. Hence, the film quality is dependent on the local relative humidity. It is important to maintain the relative humidity value of local ambience to less than 45% during the process of spin-coating and subsequent heating-cooling.

A pulse-modulated CW laser source of wavelength 1070 nm (SPI Lasers) has been used in this study. The laser was operated in pulsed mode with microsecond pulses. The laser system comprise of a fiber laser, an optical fiber cable for beam delivery, a focusing lens and an X–Y translation stage for raster scanning. The average spot size of the focused laser beam was measured to be 16.7 µm from optical microscope images at low pulse repletion rate. The output power of the laser is modulated by the pulse length selected. The maximum output power of the laser was kept fixed at 12.5 W. However, the actual output power delivered depends on the pulse duration and pulse repetition rate used. The average power density of the focused laser beam varies between 2.3×10^5 – 6.8×10^5 W/cm^2 for pulse lengths varying between 9 and 13 µs assuming 16.7 µm of spot size.

The laser source being a CW laser with pulse modulation by a chopper, the pulse duration can be varied from approximately 8 µs to 1 ms. For a fixed pulse repetition rate, the pulse length is controlled by the duty cycle ratio. The pulse length was varied between 8 and 13 µs while the pulse repetition rate of 10 kHz was used. Samples were prepared during the initial experiments with a pulse repetition rate of 8.3 kHz and therefore, some results obtained with 8.3 kHz and pulse length values of 9.5 µs is also reported. Laser doping was successful for these process parameters. However, it is difficult to characterize cylindrical laser doped channels, as presented in Fig. 1, fabricated by laser doping at points with the process conditions mentioned above. Hence, the samples were raster scanned in different scan speeds and pulse lengths for subsequent characterizations.

For surface morphology study, four probe measurement, concentration-depth profiling, lifetime measurement and cross-sectional transmission electron microscopy (TEM) study, laser beam was raster scanned on the surface with a spacing of 5 µm to ensure beam overlapping. For cross-sectional SEM-EBIC imaging, two laser doping steps were used. The first laser doping step was performed over a SOD film coated substrate with a scan speed of 60 mm/s and a pulse length of 9.5 µs at 10 kHz. The spacing between laser beam scanning lines was kept at 5 µm to ensure laser beam overlap during raster scanning. This